Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Influence of Heterogeneities on Chemical & Microbial Transport Predictions: Laboratory and Field Studies

Jim Szecsody

Pacific Northwest National Laboratory

Richland, Washington, USA

Battelle

Coupled Microbial Degradation/Transport

Ellyn Murphy
Tom Resch, Jerry Phillips (exp.)
Jim Szecsody, Brian Wood, Tim Ginn (modeling)

Question:

Can we predict the dynamics of microbial sorption coupled with biodegradation? (degrading -> desorb)

- microbial distributions become more homogeneous with electron donor/acceptor injections?
- can heterogeneities be characterized?

Methods:

- batch, 1-D, Heterogeneous 2-D laboratory experiments
- reactive transport modeling

Coupled Processes

- if not degrading, Kd = 100 (microbial isolate CN32)
- if degrading, Kd decreases with microbial activity:

  lactate + oxygen -> acetate

  lactate + nitrate -> acetate + nitrite

a1 $$\frac{d\ \mathrm{oxygen}}{dt} = -\frac{mu1}{y1}\cdot m\cdot f1\cdot\left[\frac{d}{kd1+d}\right]\cdot\left[\frac{a1}{a1+ka1}\right] - b1\cdot a1$$

a2 $$\frac{d\ \mathrm{nitrate}}{dt} = -\frac{mu2}{y2}\cdot m\cdot f2\cdot\left[\frac{d}{kd2+d}\right]\cdot\left[\cdot\frac{a2}{a2+ka2}\right]$$

d $$\frac{d\ \mathrm{lactate}}{dt} = -\frac{mu1}{y1}\cdot m\cdot\left[\frac{d}{kd1+d}\right]\cdot\left[\frac{a1}{a1+ka1}\right] - \frac{mu2}{y2}\cdot m\cdot\left[\frac{d}{kd2+d}\right]\cdot\left[\cdot\frac{a2}{a2+ka2}\right]$$

microbial sorb, desorb:

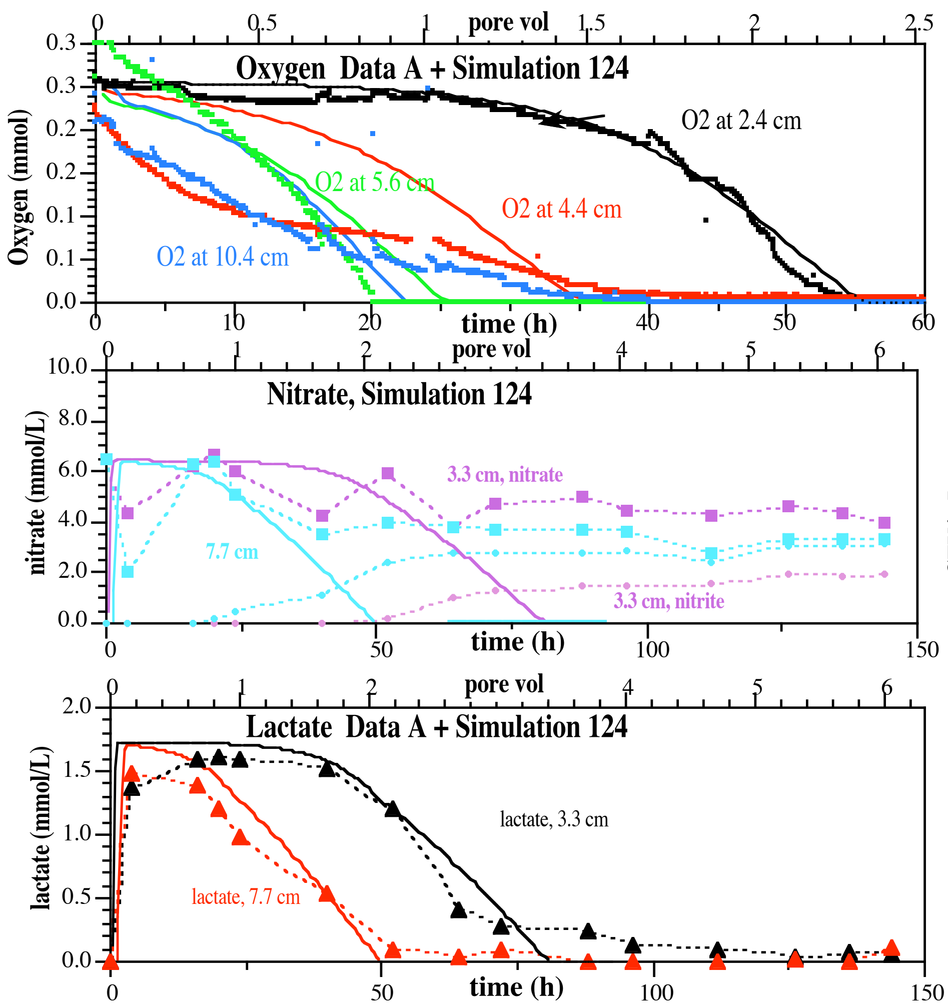
mm $$\frac{d\ \mathrm{mobmicrobes}}{dt} = mu1\cdot m\cdot\left[\frac{d}{kd1+d}\right]\cdot\left[\frac{a1}{a1+ka1}\right] + mu2\cdot m\cdot\left[\frac{d}{kd2+d}\right]\cdot\left[\cdot\frac{a2}{a2+ka2}\right] - k_f F\ m + k_b\ im$$

im $$\frac{d\ \mathrm{imobmicrobes}}{dt} = mu1\cdot im\left[\frac{d}{kd1+d}\right]\cdot\left[\frac{a1}{a1+ka1}\right] + mu2\cdot im\left[\frac{d}{kd2+d}\right]\cdot\left[\cdot\frac{a2}{a2+ka2}\right] + k_f F\ m - k_b\ im$$

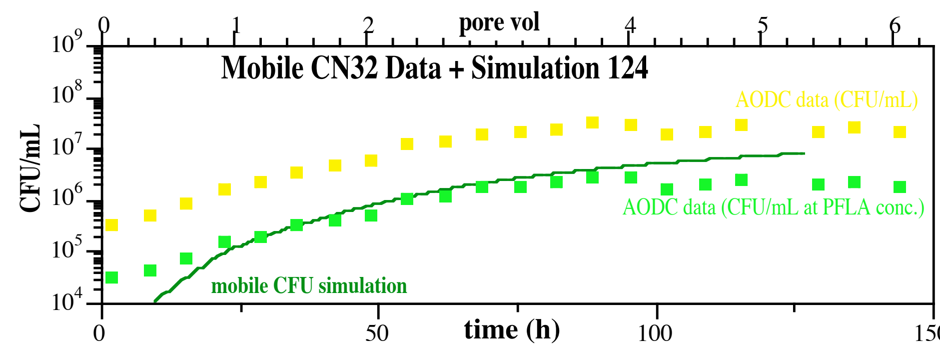
$$F = \left[1 - \left[\frac{d}{kd1+d}\right]\cdot\left[\frac{a1}{a1+ka1}\right]\right]\left[1 - \left[\frac{d}{kd2+d}\right]\cdot\left[\cdot\frac{a2}{a2+ka2}\right]\right]$$

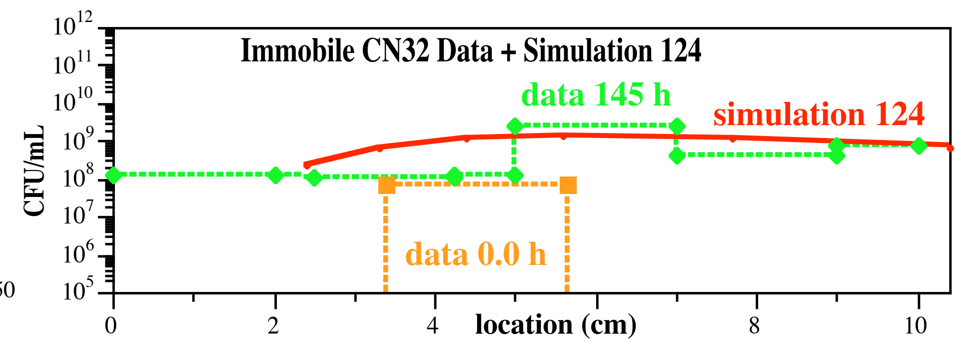
Microbial Activity in 1-D System

- biodegradation generally predicted (2 acceptors)



- microbial downgradient movement with growth predicted

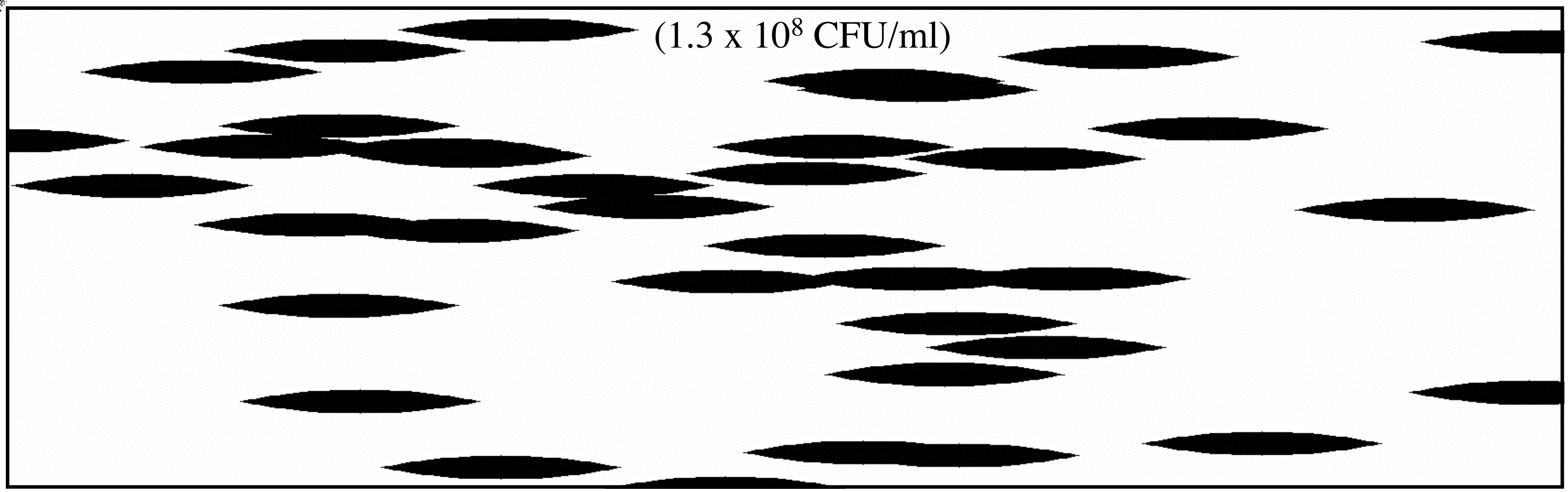




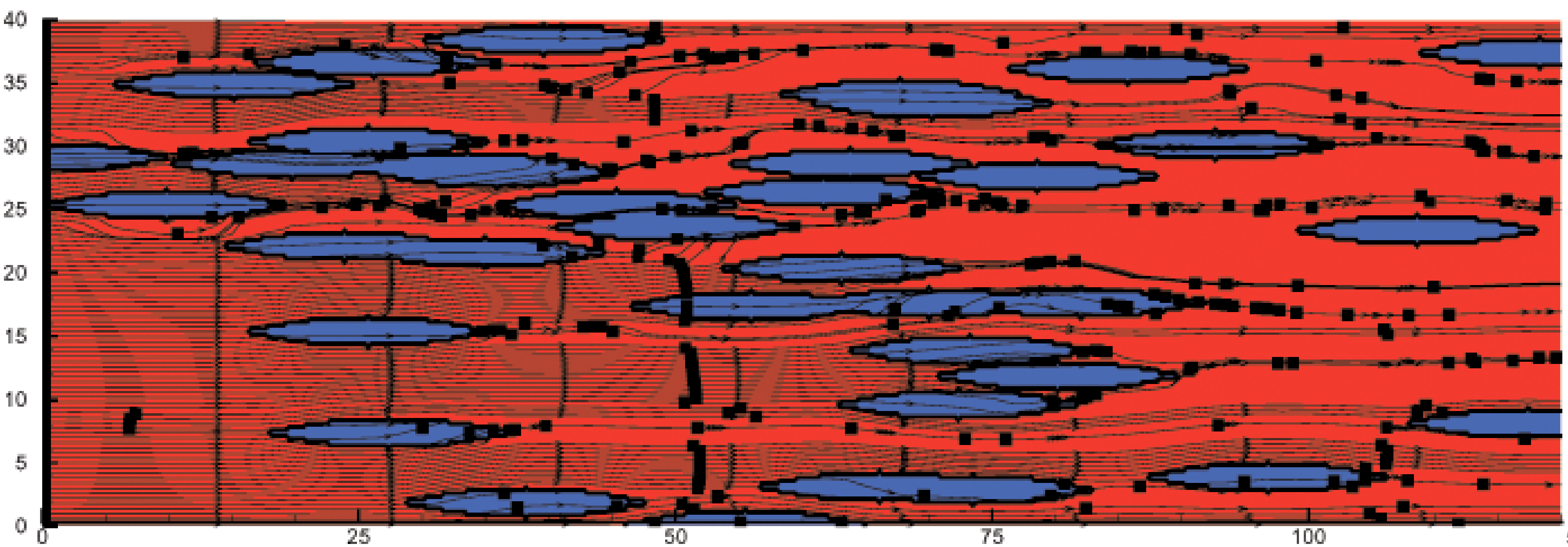
- immobile CN32 data: need more discrete sampling

2-D Experimental/Modeling System

Flow Cell Packing: CN-32 microbes only in (35) low-K lenses (16.75% of total volume):

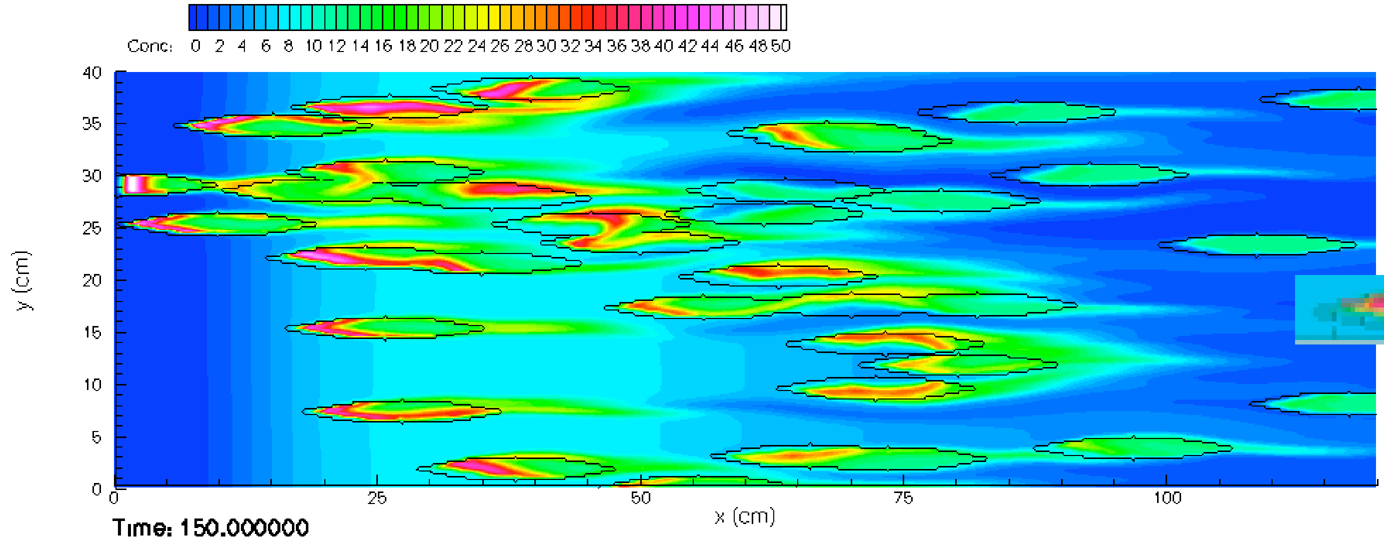


Flow Field

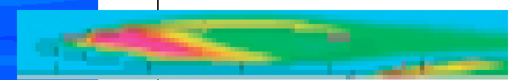


2-D Model: Testing Coupling Process

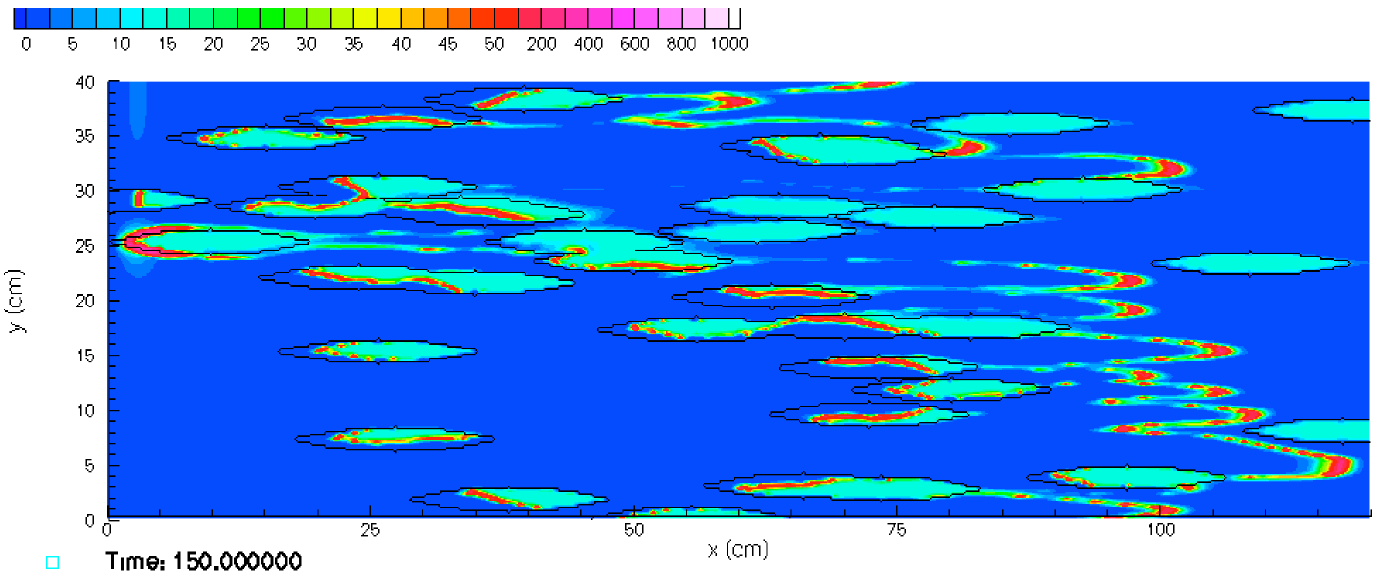
Constant Microbial Sorption (Kd = 100): inclusions 39% growth, high-K media, 15x



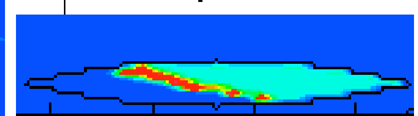
low-K pattern:



Coupled Sorption/Deg. (Kd = 100): inclusions 21% growth, high-K media, 9x



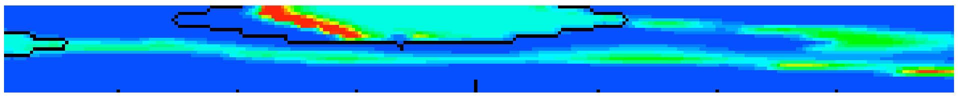
low-K pattern:



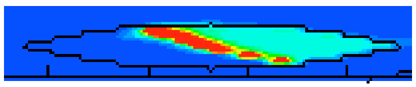
growth zones more discrete

Coupled Process Modeling: Characteristic Growth Patterns

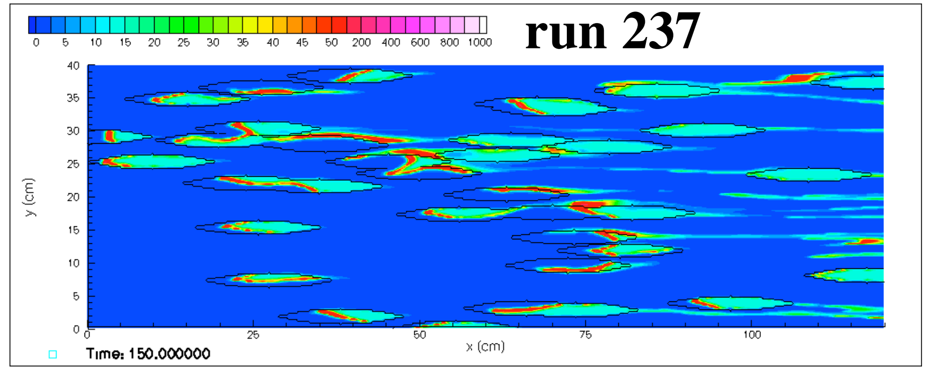
- Continuous downgradient “streaks”
  (low conc. , high velocity injection)



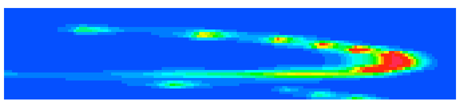
high-K pattern



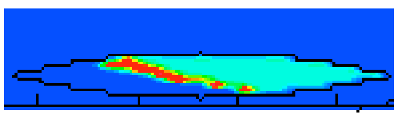
low-K pattern



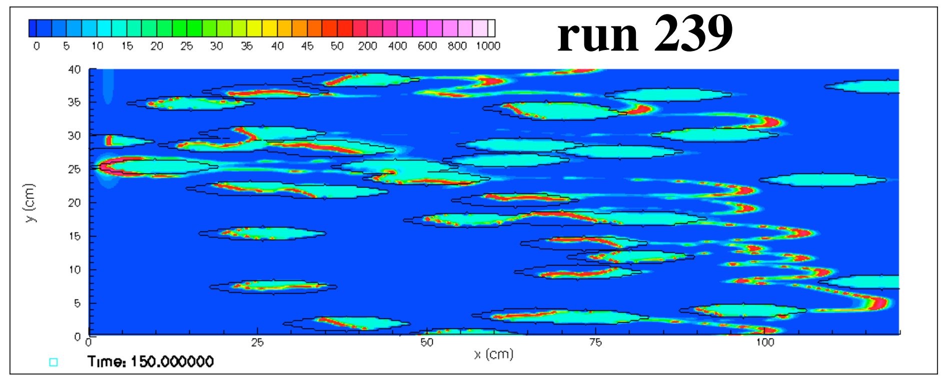
- Discontinuous downgradient "zones"
  (high conc., low vel. pulse)



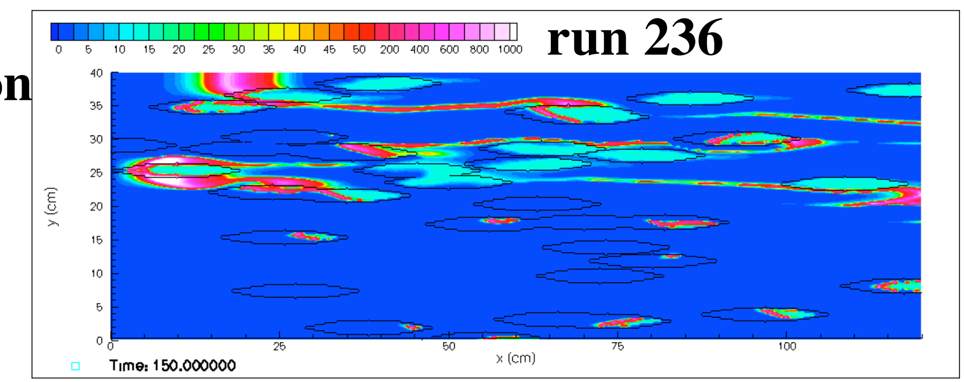
high-K pattern



low-K pattern

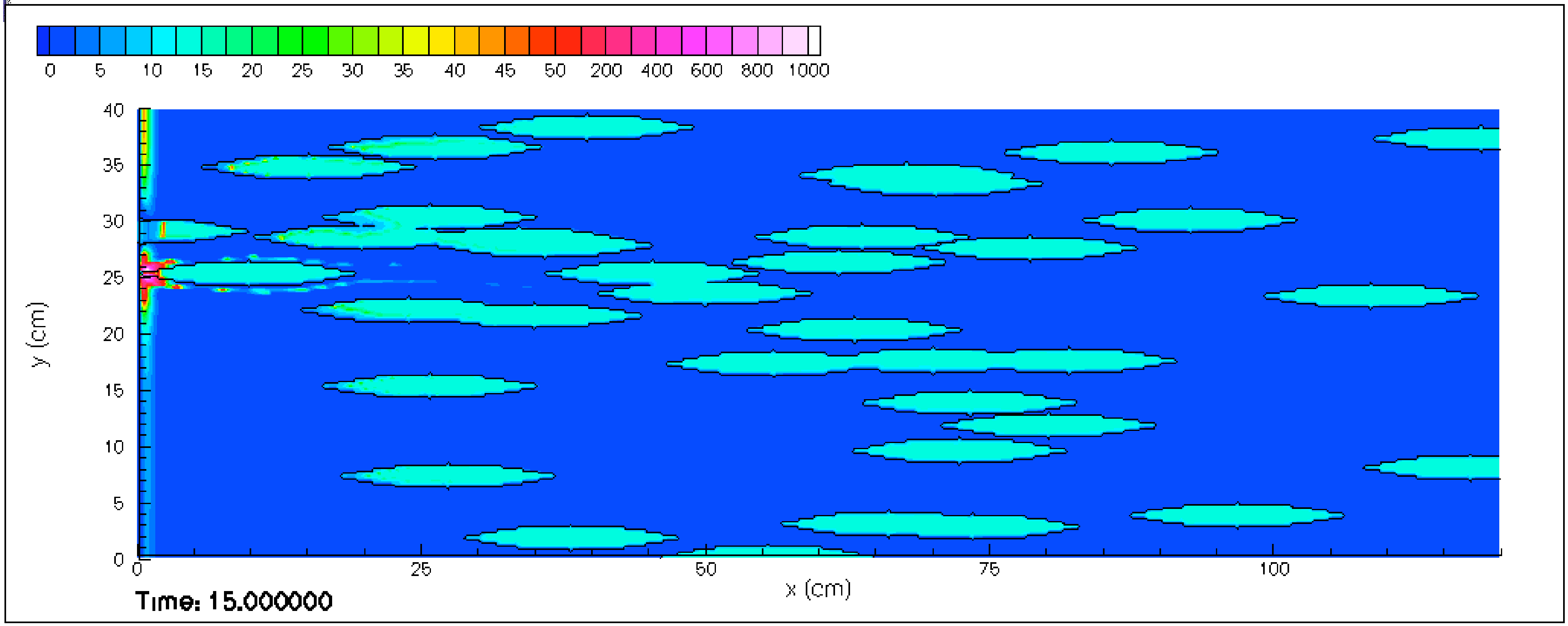


- Far field advection
  (from high conc., continuous injection



30% of biomass advected out of system

Coupled Process Modeling: Immobile Microbial Population Simulation



Predicting Coupled Microbial Degradation/Transport

- desorption coupled to degradation enables far field transport of microbes
- differing injection strategies produce differing pattern:
  - excess nutrients and flow: far field migration
  - fast flow, low conc.: continuous microbial deposition
  - short, high conc. pulse: discontinuous microbial deposition (i.e., nutrient pulse relative to inclusion size and flux)
- may be able to characterize heterogeneities to some extent by differing injection strategies

(coupled process quantified in idealized laboratory-scale system with intense sampling strategy and simulations)

Heterogeneity and Field-Scale Permeable Barriers

John Fruchter, Vince Vermeul (PIs), Chris Murray, Yulong Xie (geostatistics)
Mark Rockhold, Mark Williams (modeling), Jim Szecsody (geochemistry)

Questions:

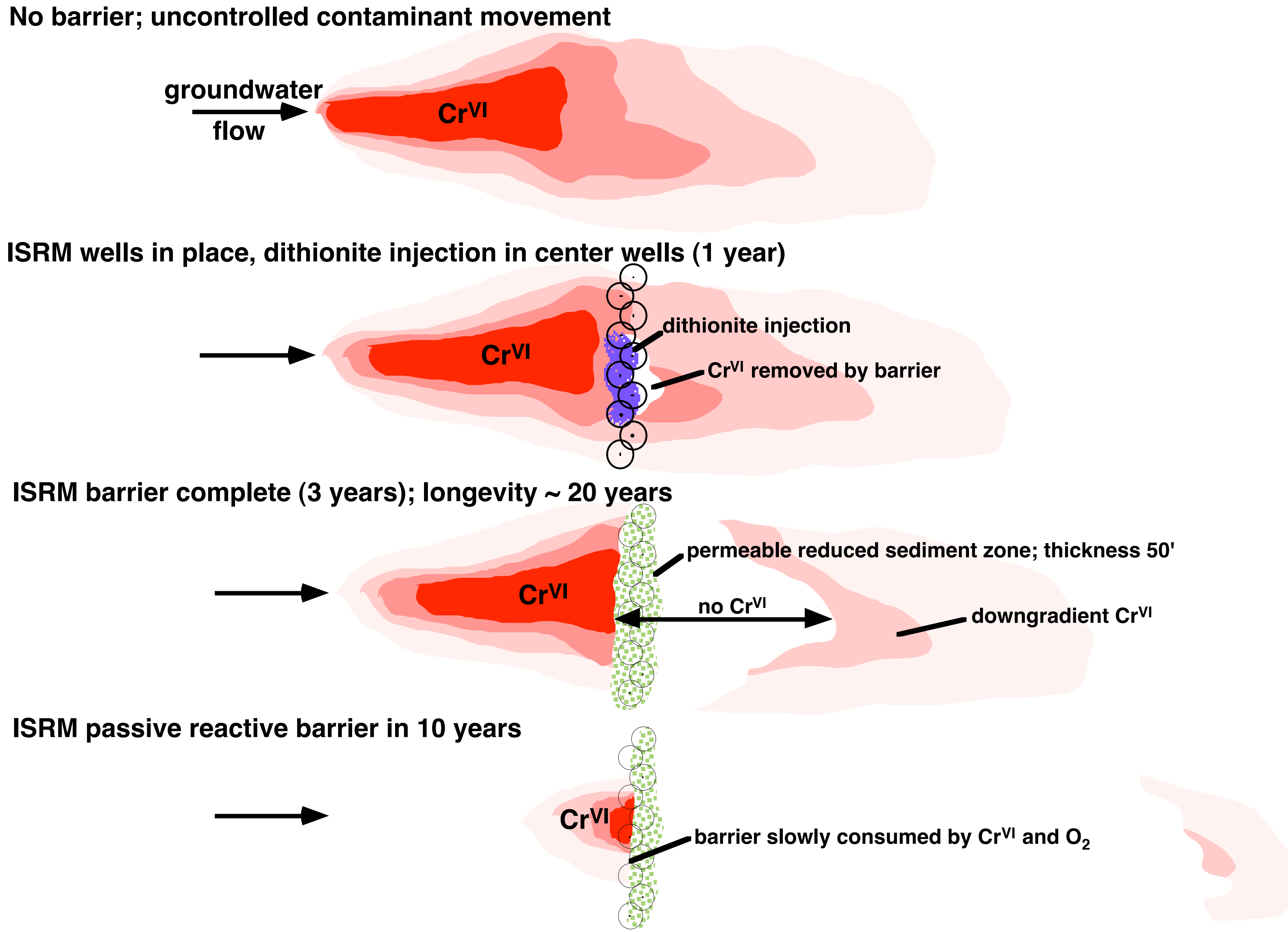
What is the influence on a chemical redox-reactive subsurface barrier by:

- scale of heterogeneity
- anisotropy

Methods:

- field scale characterization, geostatistics, simulations
- comparison with field scale injection data, long-term barrier performance

Reactive Redox Barrier Concept



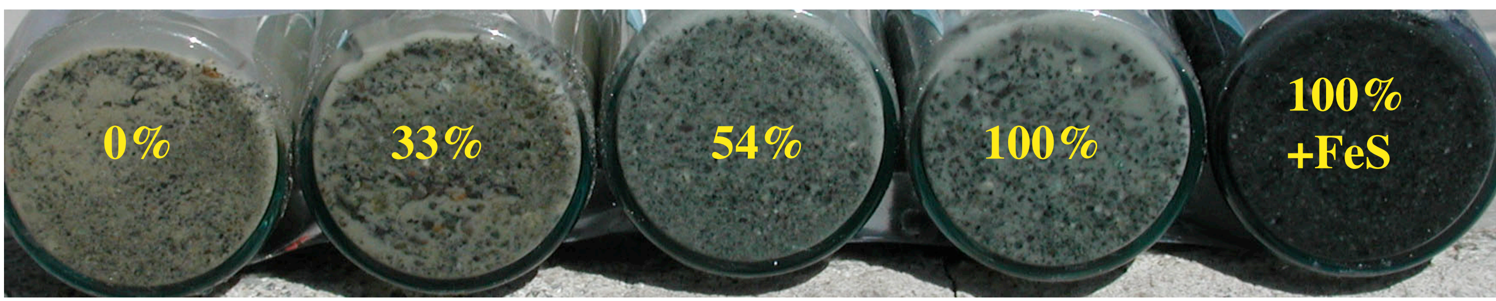
- **barrier is slowly oxidized over decades**

Iron Phase Changes During Reduction

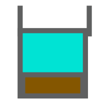
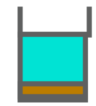
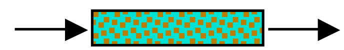
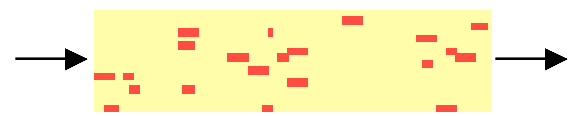
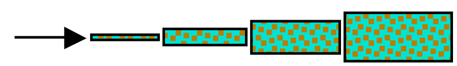
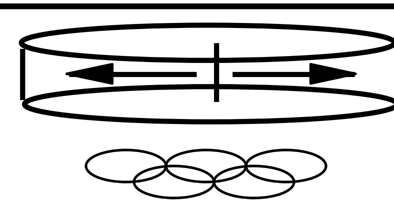
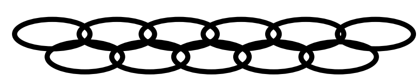
sediment	$Fe^{II}CO_3$	ads. Fe^{II}	am-Fe^{III}	crys.-Fe^{III}
	Fe^{II}		Fe^{III}	
untreated	18	0.2	86	140
reduced	36	155	38	106
red./oxidized	26	0.0	75	150

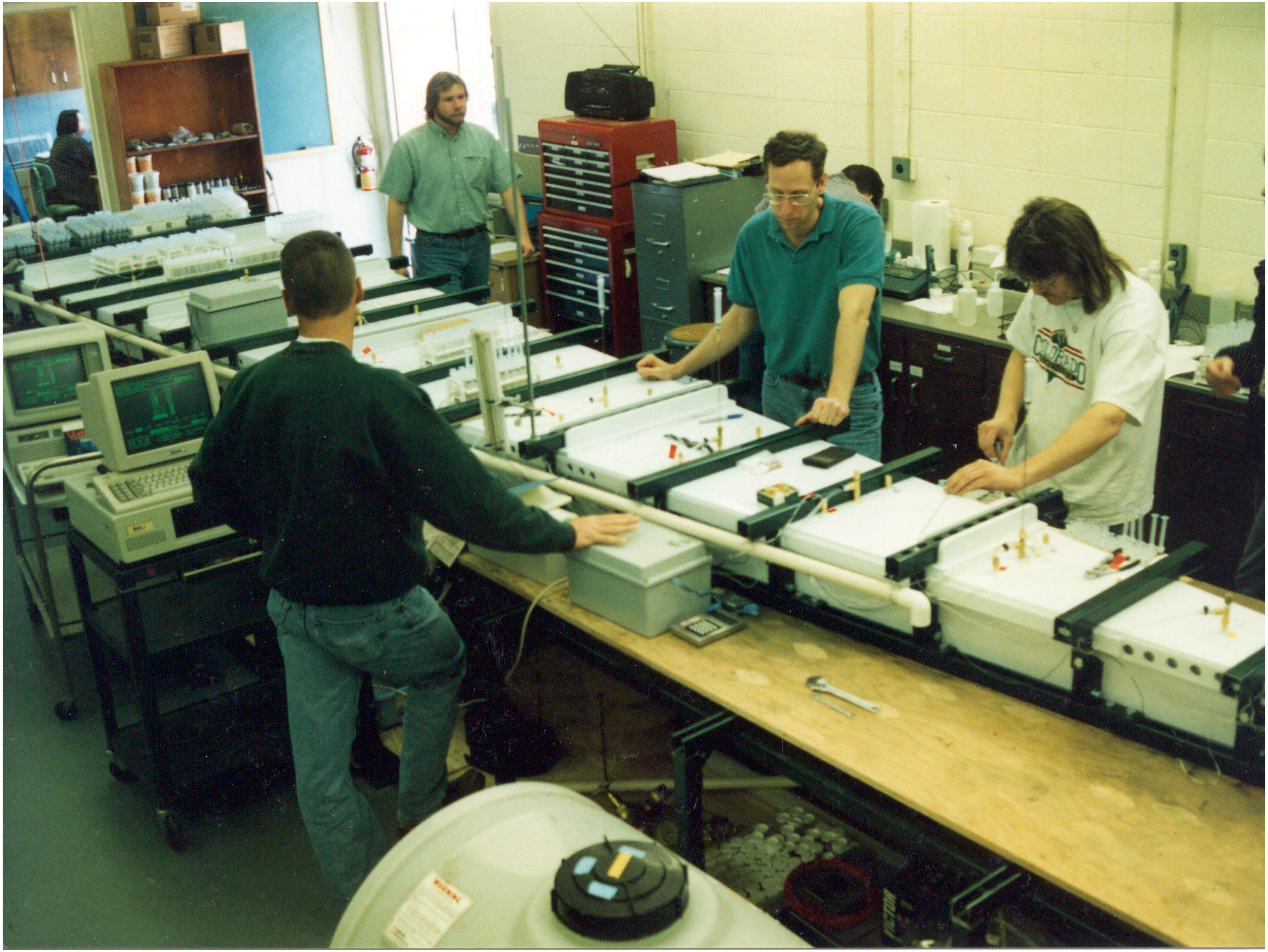
(all μmol Fe/g)

- 80% of Fe^{II} reduced is adsorbed Fe^{II}, <20% siderite
  all adsorbed Fe^{II} and some siderite is oxidized by O_2

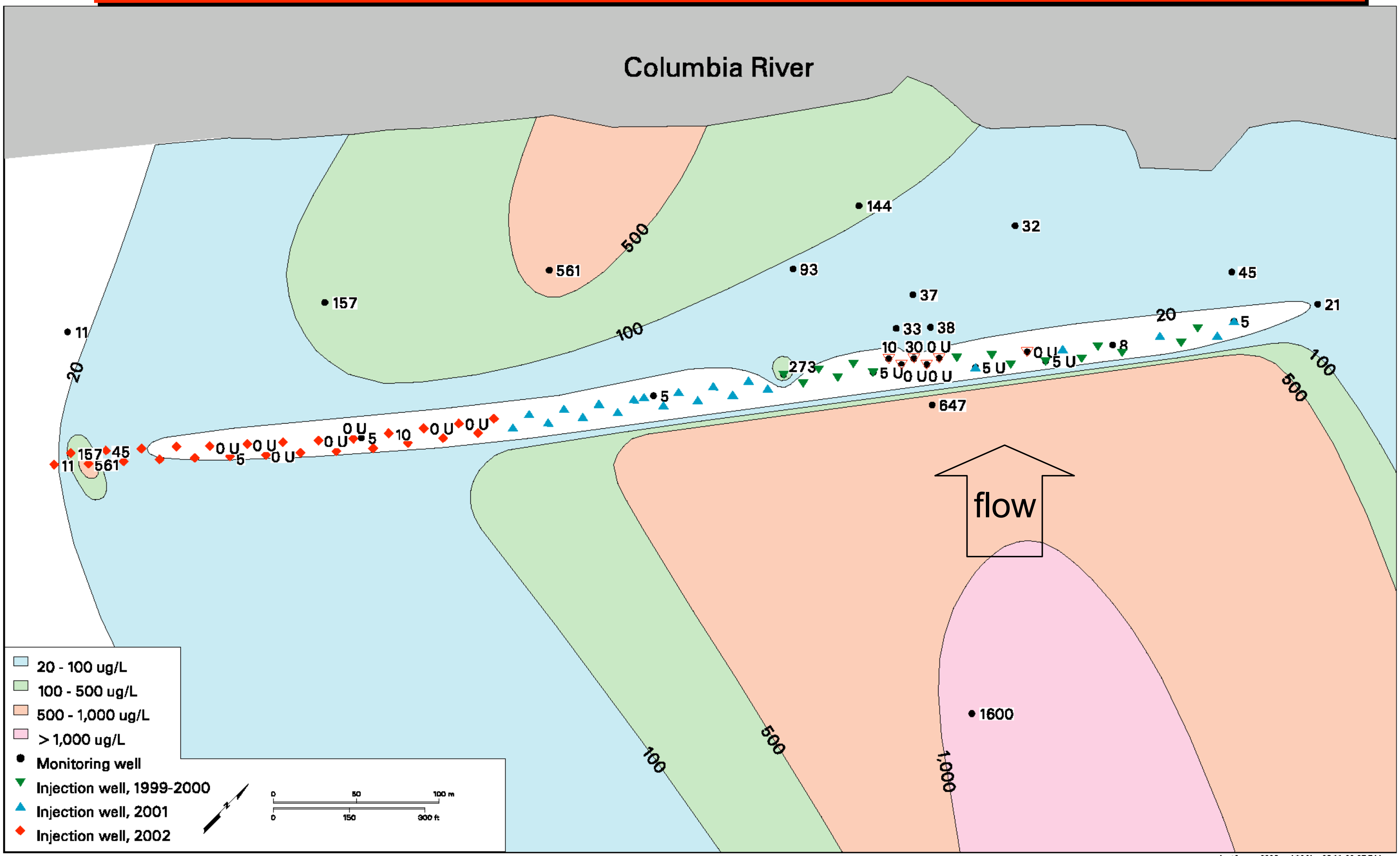


Scale of Research

	Objective	Experiment
Bench Scale	• Identify/quantify geochemical reactions • Interactions of multiple reactions • Reactivity in flowing columns • Reactive Transport with Particle-Scale Heterogeneity	 **Batch - Artificial Sediments**  **Batch - Natural Sediments**  **1-D Column**
Intermediate Scale	• Reactive Transport with Chemical Heterogeneities • Reaction rates in radial flow field • Aquifer Clogging, Clay movement, Test field-scale operations	 **2-D (1 m)**  **Quasi-radial (15 m)**  **Radial (7 m)**
Field Scale	• Reactivity/Conceptualization in natural system, dense fluid injection • Application in Contaminated Aquifer	 **Single Well Injection/Recovery, 14 monitoring wells (10 m)**  **Multiple Well Injection/Recovery (600 m)**


COLORADO

Chromium in Groundwater – ISRM Barrier Hanford 100D Area – September, 2002

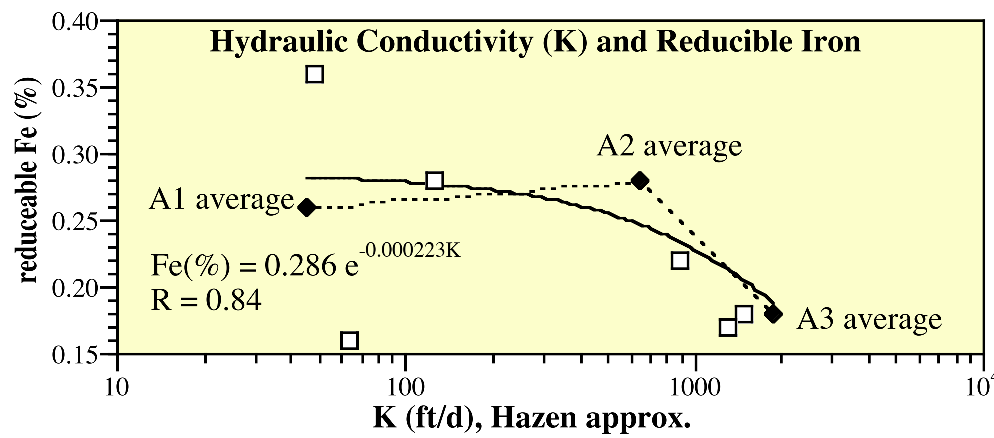


ISRM Hanford 100D Area Barrier Issue

Issue:
Chromate breakthrough after 6 years in one location

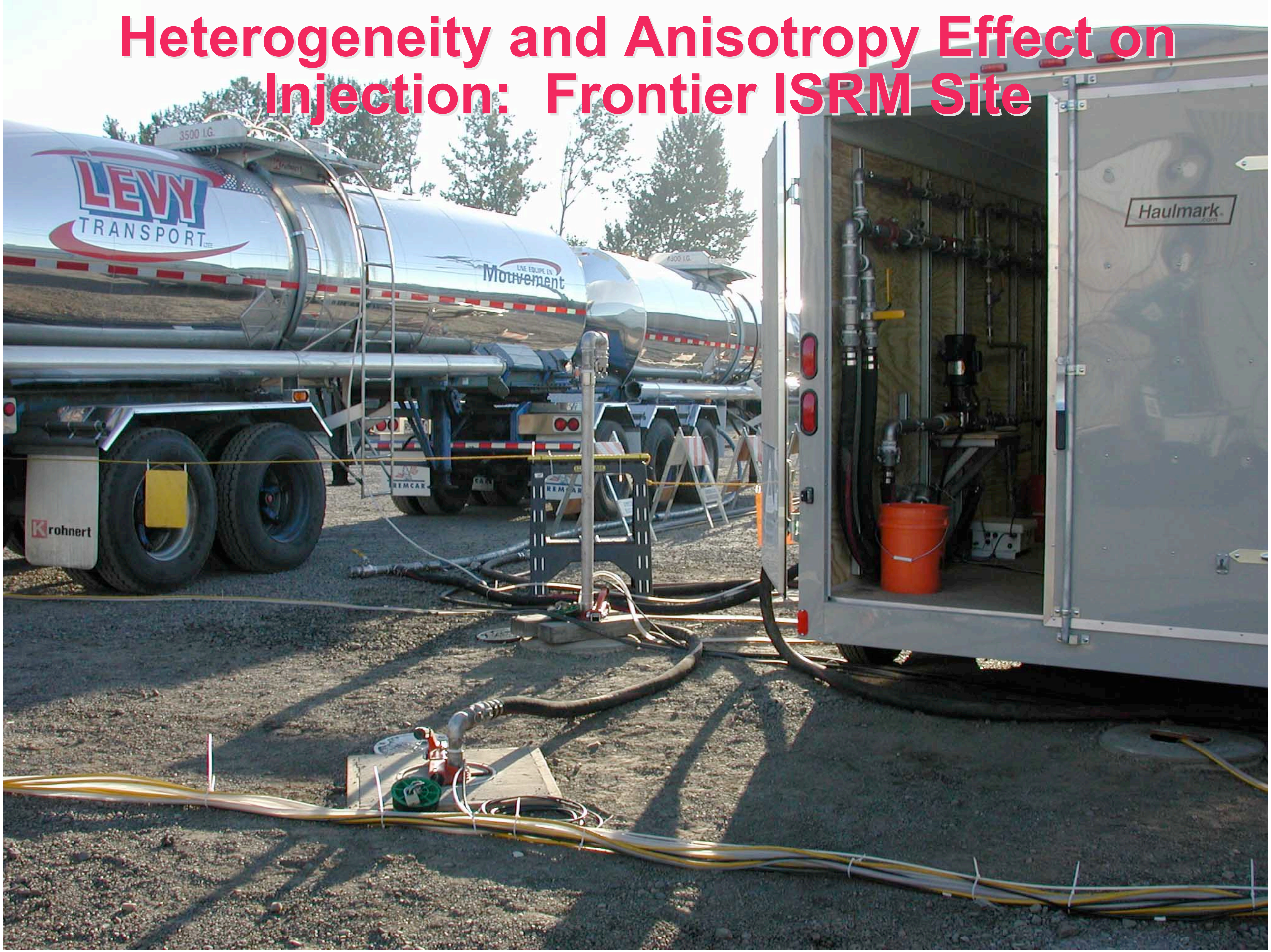
Potential Causes:
- air rotary drilling prematurely causing barrier oxidation
- high-K, low-Fe zone extends through barrier; natural or air-injection caused (i.e., large scale heterogeneity)

Path forward:
- re-reduce, monitor barrier for years



(unknown effect of drilling)
(insufficient heterogeneity characterization)

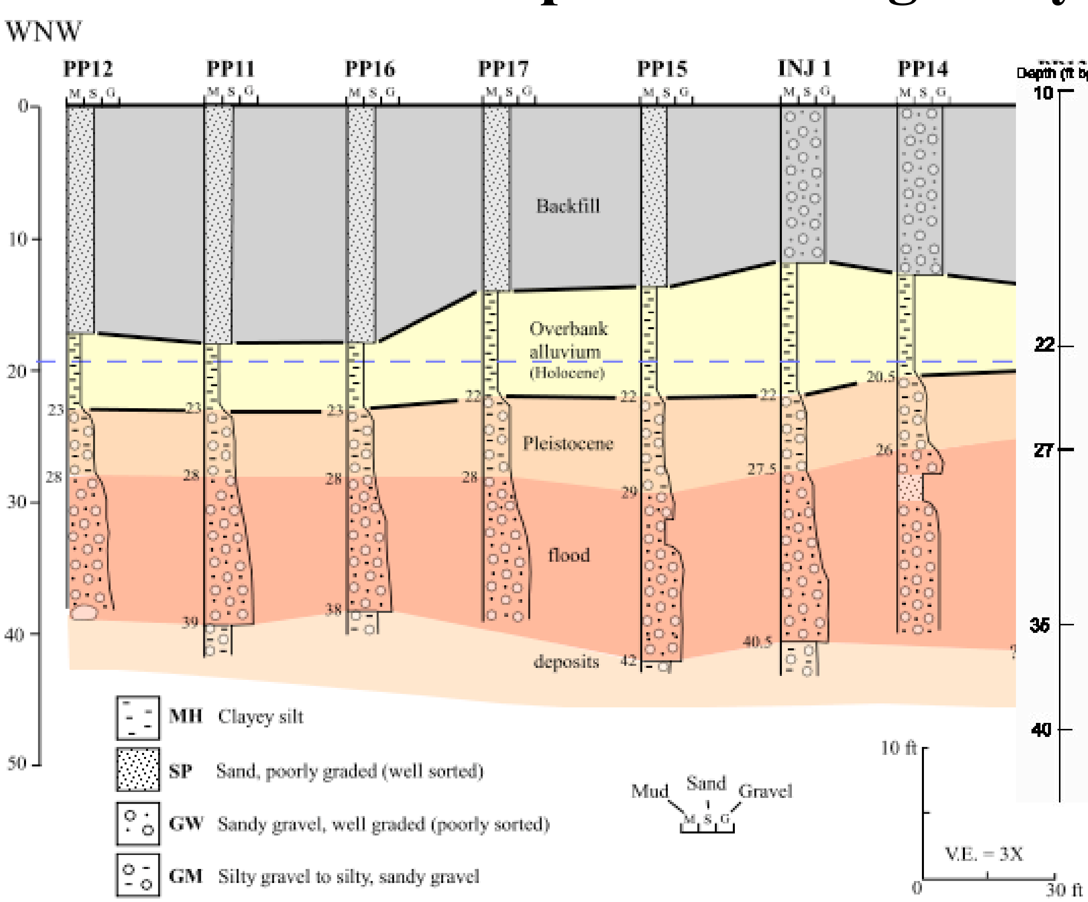
Heterogeneity and Anisotropy Effect on Injection: Frontier ISRM Site



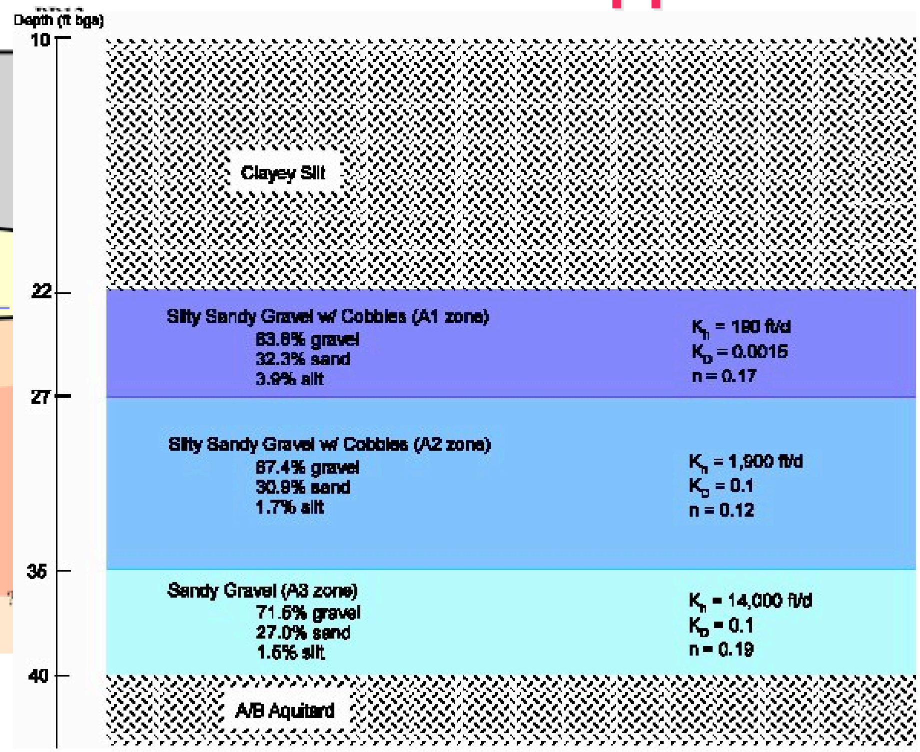
Frontier Chrome Site

Objective: prevent offsite migration of chromate

Issues:
- layers: A1 high chrome/low-K,
  A2: low chrome/high-K
- spatial heterogeneity

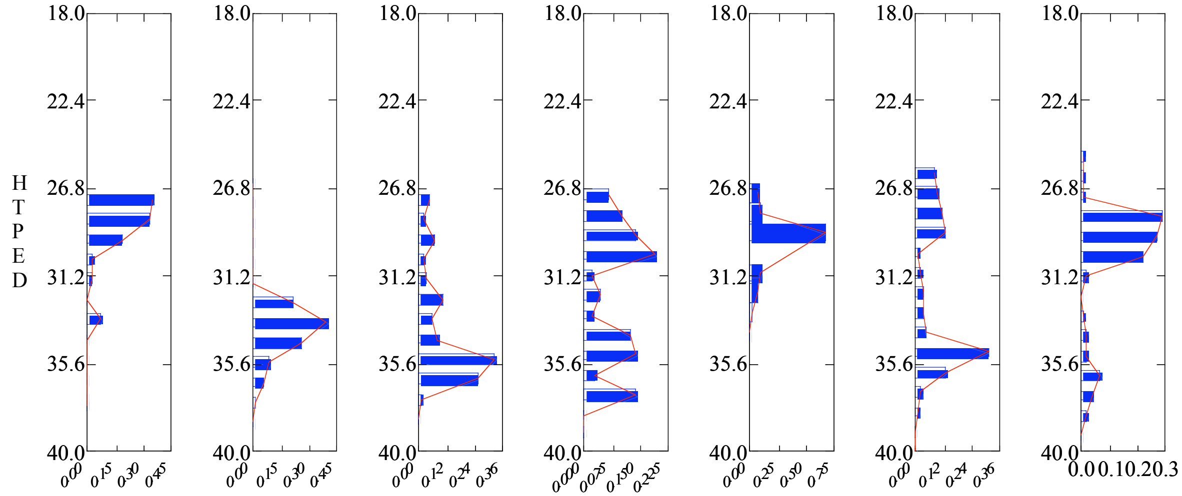


is this a valid approach?

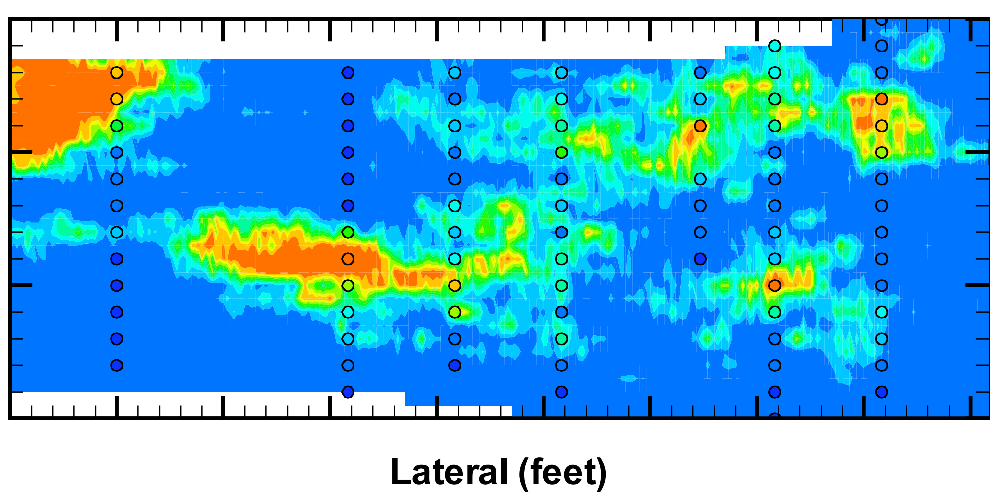


Heterogeneity Approach

Characterize Heterogeneity: borehole flowmeters - relative K



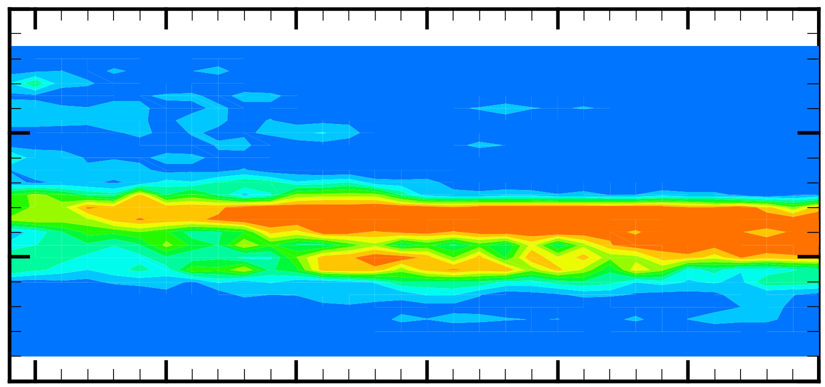
Synthesize 3-D K_{sat}/Fe distribution: assume correlation area



Simulation Approach

Average K_{sat} field from 100 realizations

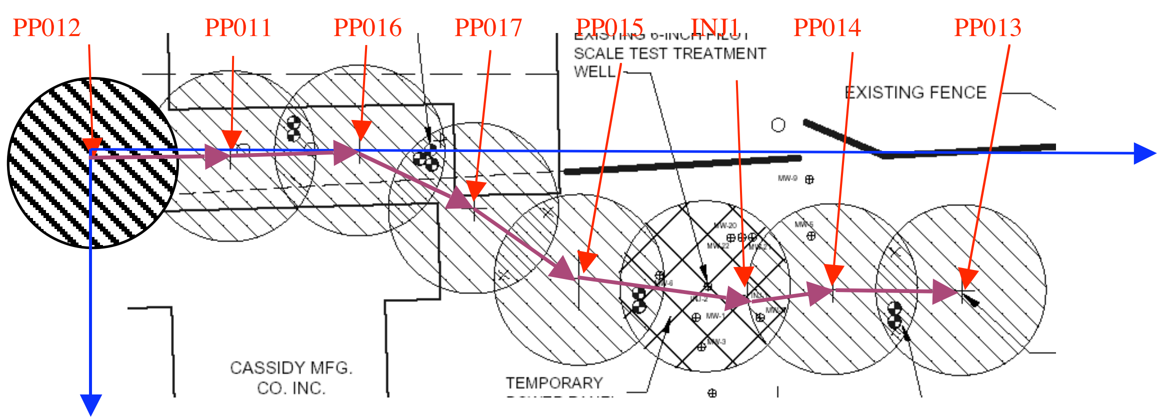
Single well (2-D radial) simulation to address injections



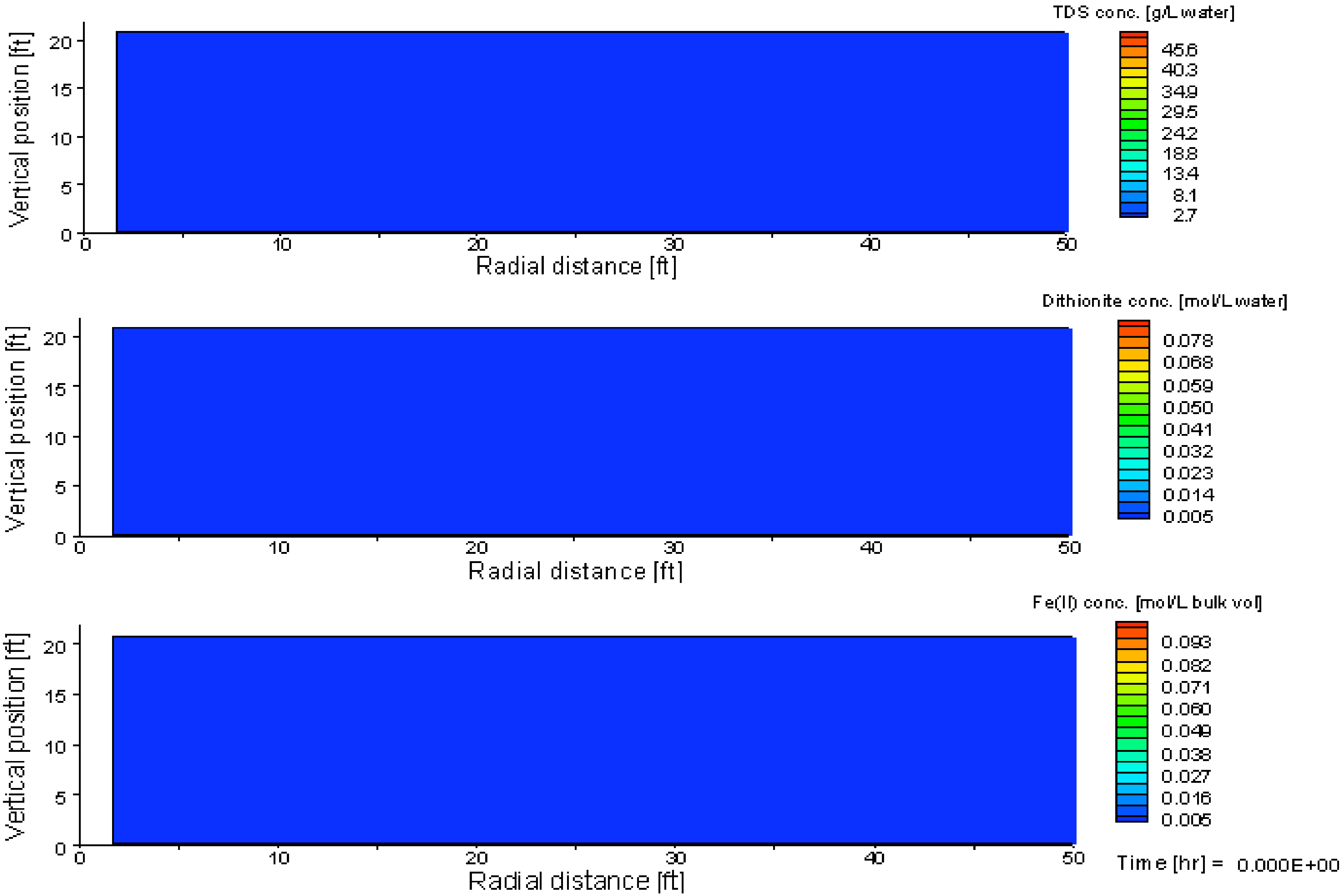
single well flow field

3-D simulation to address barrier longevity

Figure 2 ISRM Barrier Installation Plan map

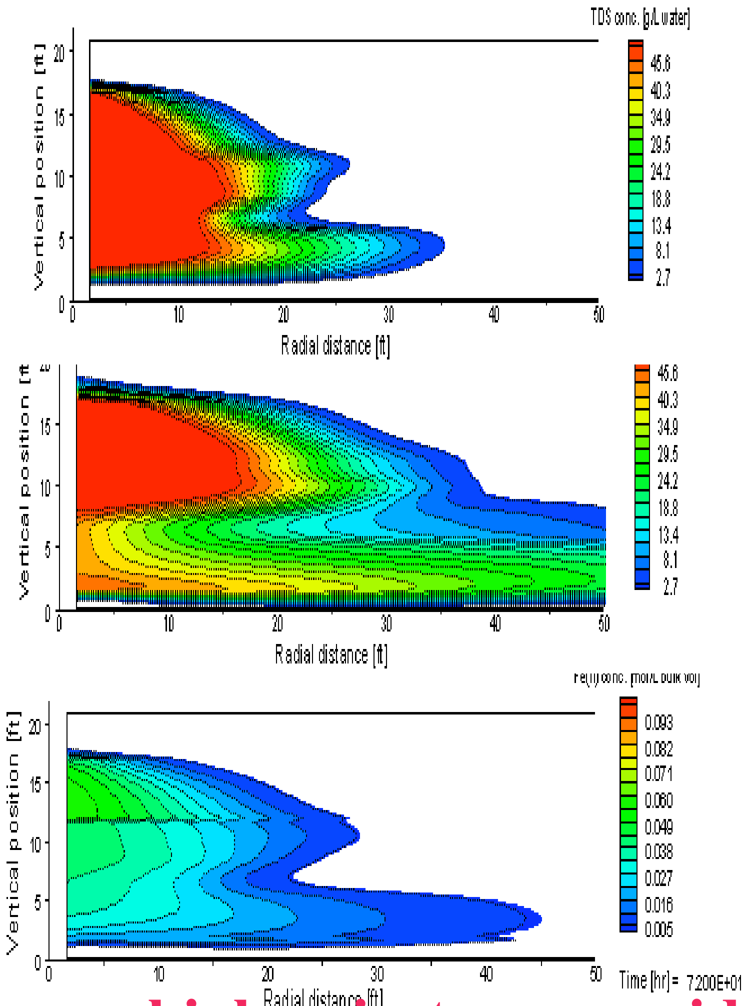


ISRM Design Simulation for Frontier Hard Chrome Site, Vancouver, WA .
Case: Fixed5, modified rates and conc. (PP016): 10 gpm, 0.1 molar dithionite, 0-21 hr injection into unit A1 (layered, Kh=100*Kv), and 30 gpm, 0.1 molar dithionite, 6-21 hr injection into unit A2 (layered, Kh=100*Kv).

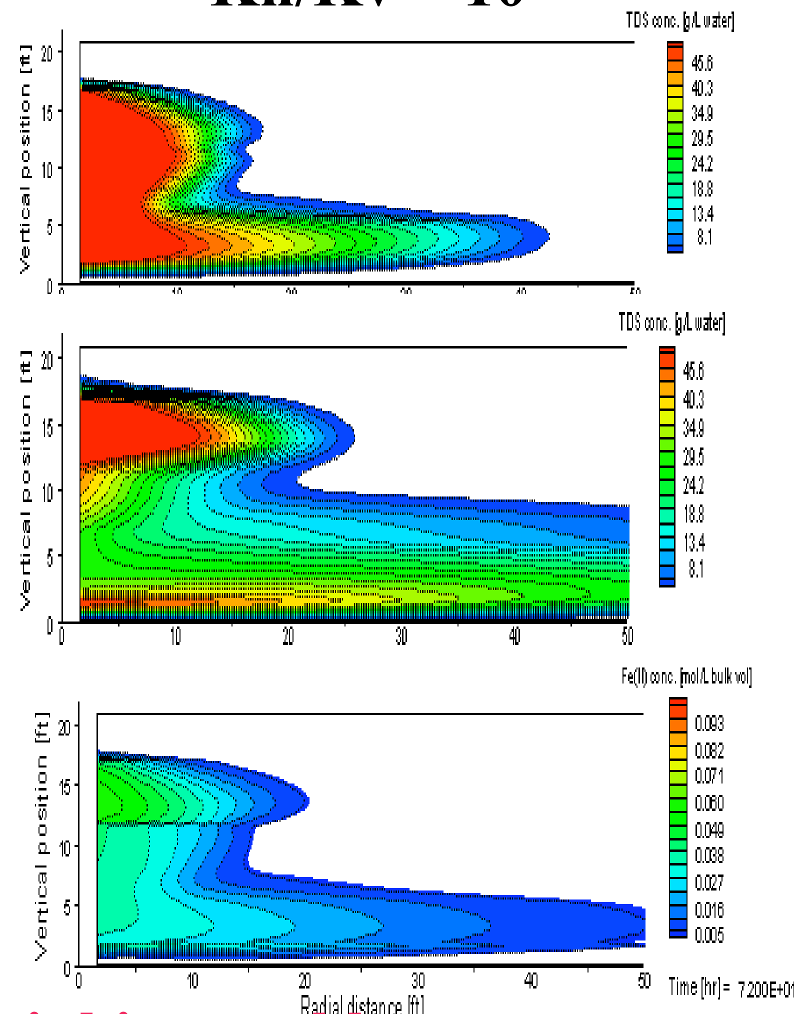


Anisotropy

Kh/Kv = 100



Kh/Kv = 10



dith.
6 h

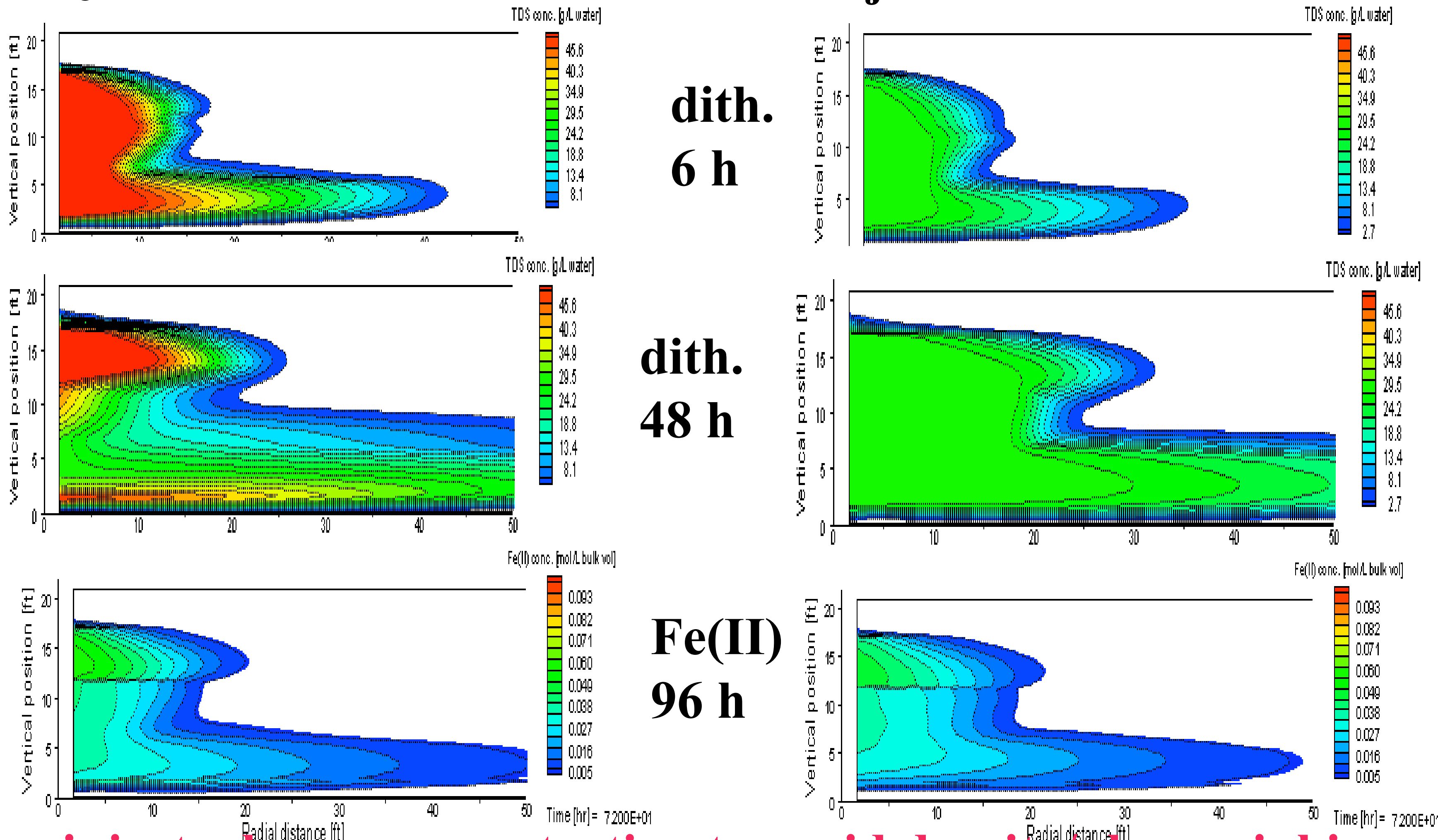
dith.
48 h

Fe(II)
96 h

- high anisotropy avoids plume sinking problem
- pump test data indicates Kh/Kv = 100+ (large scale data)
- dense liquid injection data indicates Kh/Kv = 10

Plume Sinking and Heterogeneity

inject 0.08 M dithionite | **inject 0.04 M dithionite**



- inject a lower concentration to avoid density/plume sinking
- injection data indicates more sinking than simulations (heterogeneities not as continuous?)

In Situ Reactive Barrier Design

- lateral extent of high-K/low-Fe layers could affect long-term barrier performance; open question

- multi-well anisotropy data insufficient for prediction of single-well dense plume injection (scale of data)

- even with 14 wells within 120 ft, insufficient heterogeneity characterization to address lateral extent of high-K layers

(coupled processes not quantified at field scale, even with intense sampling strategy and simulations)